Small Magnetic Polaron Picture of Colossal Magnetoresistance in Manganites

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We present a small-but-sizeable magnetic polaron picture where transport at high temperatures is activated while at low temperatures it is band-like. We show that both double exchange and finite bandwidth effects are important to understand colossal magnetoresistance as well as the coincidence of the metal-insulator and the ferromagnetic transitions in manganites. The magnetic transition is explained using band-like motion of the polarons.

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Studies on perovskite manganites of the form $A_{1-\delta}B_{\delta}MnO_3$ (A=La, Pr, Nd, etc.; B=Sr, Ca, Ba, etc.) have yielded a variety of rich phenomena as a function of doping δ–coexisting orbital ordering and layered antiferromagnetism at low doping, simultaneous metal-insulator (MI) and paramagnetic-ferromagnetic transitions at intermediate doping ($\delta \sim 0.2 - 0.4$), and charge ordering at higher doping ($\delta \sim 0.5$) [1]. To explain the magnetic ordering, de Gennes [2] some time ago had proposed double exchange mechanism wherein, on account of strong Hund's coupling between the spin of a mobile hole and the spin of the localized electrons, the hopping integral of the itinerant hole is reduced by half of the cosine of the angle between the 3/2 spins of the localized electrons on neighboring sites. However it was recognized by Millis et al. [3] that this mechanism itself is not sufficient to explain colossal magnetoresistance (CMR). Millis and co-workers have proposed a model [4] which uses Jahn-Teller coupling between electrons and nuclei. However this model does not seem to yield satisfactory results away from half-filling. Röder et al. have also emphasized the importance of Jahn-Teller coupling in understanding these manganites [5]. Earlier on De Teresa et al. [6] have reported evidence for sizeable magnetic polarons above the ferromagnetic transition temperature. Recently worledge et al. [7] have demonstrated that their high temperature resistivity data fits well to an adiabatic small polaron model. All in all there is growing evidence for a small magnetic polaron picture to explain CMR.

In this paper we study CMR phenomena in perovskite manganites (for $\delta \sim 0.2 - 0.4$) by considering the carriers as adiabatic small-but-sizeable magnetic polarons whose high temperature behavior is hopping type and low temperature behavior is metal-like. Our notion of small-but-sizeable polaron is similar to that of a nearly-small polaron introduced by Eagles [8]. Our treatment builds on the work of Gosar [9], who included finite band width effects by actually considering a small-but-sizeable polaron whose wavefunction extends to the nearest neighbors. Due to Hund's coupling the electrons on the nearest neighbors also have the same polarization. Our model includes effects due to electron-phonon coupling, on-site Hund's coupling between itinerant holes and localized electrons, coupling between nearest neighbor localized spins, and strong on-site repulsion between two itinerant holes. To understand MI transition we simplify the Hamiltonian by accounting for the Hund's coupling through the double exchange hopping term [2]. We show that in the absence of a magnetic field the double exchange and finite bandwidth effects can make the MI transition coincide with the magnetic transition. We also find that in the presence of a magnetic field both double exchange and finite band width effects lower the resistivity and shift its peak to higher temperatures and thus can lead to CMR.

Within a mean-field approach, we calculate the magnetization (M) of the localized spins as well as the polarization (Δn) of the itinerant hole spins. The magnetization M is a function of the external magnetic field and, due to the strong Hund's coupling, of also the polarization Δn. The polarization Δn is in turn a function of M and the external field. Thus the two (M and Δn) are coupled and have to be solved simultaneously for a given density of holes. We have studied the magnetization at different doping values, for both with and without external magnetic fields, and found that our M values are qualitatively in agreement with experimental results [10]. Furthermore our magnetoresistance values also compare favorably with experimental ones [10].

Our starting total Hamiltonian is given by

$$H_T = H(t) + H_{sp} + H_{ph} \tag{1}$$

where

$$H(t) = t \sum_{\langle ij \rangle, \sigma} c^{\dagger}_{i,\sigma} c_{j,\sigma}, \tag{2}$$

$$H_{ph} = \sum_{\vec{q}} \omega_{\vec{q}} a^{\dagger}_{\vec{q}} a_{\vec{q}} + \sum_{j,\vec{q},\sigma} n^{\sigma}_{j} e^{i\vec{q}\cdot\vec{R}_j} M_{\vec{q}} (a_{\vec{q}} + a^{\dagger}_{-\vec{q}}), \tag{3}$$

and

$$H_{sp} = \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j + K_H \sum_i \vec{\sigma}_i \cdot \vec{S}_i + U \sum_{j,\sigma} n^{\sigma}_{j} n^{-\sigma}_{j}.$$

In the above equations $c_{j,\sigma}$ ($a_{\vec{q}}$) is the hole (phonon) destruction operator, t is the hopping integral, $\langle ij \rangle$ corresponds to nearest neighbors, $\omega_{\vec{q}}$ is the optical phonon frequency ($\hbar = 1$), M_q is the hole-phonon coupling, J_{ij} is the strength of the spin coupling between neighboring localized (S=3/2) spins, K_H gives the Hund's coupling between localized spins and itinerant hole ($\sigma = 1/2$) spin , U is the strength of the same site repulsion, and $n_j^\sigma = c_{j,\sigma}^\dagger c_{j,\sigma}$. Furthermore the H_{ph} part corresponds to assuming a single orbital per site which on account of Jahn-Teller splitting may perhaps be justified.

To study transport we use double exchange modification and take the total Hamiltonian to be

$$H_T^{tr} = t_{DE} \sum_{\langle ij \rangle} c_i^\dagger c_j + \sum_{\vec{q}} \omega_{\vec{q}} a_{\vec{q}}^\dagger a_{\vec{q}} + \sum_{j,\vec{q}} c_j^\dagger c_j e^{i\vec{q}\cdot\vec{R}_j} M_{\vec{q}} (a_{\vec{q}} + a_{-\vec{q}}^\dagger), \quad (4)$$

where $t_{DE} = t\sqrt{(1 + M^2/M_S^2)/2}$, and M_S is the saturated magnetization. Now the mobility is given by the Einstein relation $\mu = q_e D \beta$ where q_e is the electronic charge, D the diffusivity, and $\beta = 1/k_B T$. Including finite band width corrections, as done variationally by Gosar [9], to calculate the hopping-regime diffusivity $D_{hop} = a^2/(6\tau)$ we obtain the scattering lifetime τ for a *narrow* phononic band to be

$$1/(6\tau) = F_{[A,NA]} \exp\left[-2\theta \tanh(\beta\omega_0/4)\right], \quad (5)$$

where a is the lattice constant, ω_0 is the Debye frequency, $\theta \equiv \gamma^2 \left[1 - \frac{(z+1)t_{DE}^2}{2\gamma^4 \omega_0^2}\right]$ with z being the coordination number and, for N lattice sites, $\gamma\omega_0 = M_{\vec{q}} N^{1/2}$. In the present analysis the small-but-sizeable polaron condition is $\frac{(z+1)t_{DE}^2}{2\gamma^4\omega_0^2} < 1$. In Eq. (5), F_A and F_{NA} are the prefactors for adiabatic and non-adiabatic cases with

$$F_{[A]} \equiv \frac{\omega_0}{2\pi} \frac{[1 + (M/M_S)^2]}{2}, \quad (6)$$

and

$$F_{[NA]} \equiv \frac{t_{DE}^2 \sqrt{\pi \sinh(\beta\omega_0/2)}}{\omega_0 \sqrt{\theta}}, \quad (7)$$

where the adiabatic term $F_{[A]}$ is obtained using arguments similar to those put forth by Holstein [11]. The crossover from the non-adiabatic case to the adiabatic case occurs when $F_{[NA]} > F_{[A]}$. For experimentally studied systems the adiabatic regime is of interest. Furthermore, it should be noted that we need $2\theta \text{csch}(\beta\omega_0/2) >> 1$ for Eq. (5) to be valid (for a justification in the narrow band case $\theta = \gamma^2$ see Ref. [11]). As for the diffusivity for band conduction, it is obtained by extending Gosar's work [9] and calculating the polaronic band energy [12]

$$E_{\vec{k}} = 2t_{DE} \exp\left[-\theta \coth(\beta\omega_0/2)\right] \sum_l \cos(k_l a). \quad (8)$$

The above expression is similar to the result due to Eagles [8]. Then the diffusivity for band conduction is given by

$$D_{band} = \langle |\vec{\nabla} E_{\vec{k}}|^2 \tau \rangle = 6\tau a^2 \tilde{t}^2 \frac{[1 + (M/M_S)^2]}{2}, \quad (9)$$

where $\tilde{t} = t \exp\left[-\theta \coth(\beta\omega_0/2)\right]$. Then based on Friedman's work [13] we take the total mobility (μ_T) to be the sum of the band mobility and the hopping mobility and hence the total resistivity ($1/\rho = c_h q_e \mu_T$) to be given by

$$\frac{4\pi}{c_h q_e^2 a^2 \rho} = \beta\omega_0 \left[8\pi^2 \frac{t^2}{\omega_0^2} \exp\left[-2\theta \text{csch}(\frac{\beta\omega_0}{2})\right] + \left(1 + \frac{M^2}{M_S^2}\right) \exp\left[-2\theta \tanh(\frac{\beta\omega_0}{4})\right] \right], \quad (10)$$

where c_h is the density of holes. Here it should be mentioned that, even if t and K_H are of the same order of magnitude, we can have $\tilde{t} << K_H$ so that double exchange holds.

To proceed further one needs to obtain the magnetization as a function of temperature. To this end we consider the following thermally averaged Hamiltonian

$$H_{mag} = H(\tilde{t}) + H_{sp}. \quad (11)$$

Next we note that $|J_{ij}| << K_H$ and that $U >> t$ ($\& K_H$) and hence completely project out double occupation (see Ref. [14] for details). From the above Hamiltonian H_{mag} it follows that, within a mean-field treatment, the magnetization in the presence of a magnetic field H is

$$S\frac{M}{M_S} = -\frac{\sum_{S_z} S_z \exp[-(\Phi/2 + g\mu_B H) S_z \beta]}{\sum_{S_z} \exp[-(\Phi/2 + g\mu_B H) S_z \beta]}, \quad (12)$$

where $\Phi \equiv K_H \left\{ n^\uparrow f(n^\downarrow) - n^\downarrow f(n^\uparrow) \right\}$, $f(n^\alpha) \equiv 1/(1 - n^\alpha)$, and n^α is the probability of occupation of a site by spin α hole and is given by

$$n^\alpha = \frac{1}{N} \sum_{\vec{k}} n_{\vec{k}}^\alpha \left[\epsilon_{\vec{k}}^\alpha - \Psi\sigma - \mu\right] \approx \frac{1}{\exp[-\beta(\Psi\sigma + \mu)] + 1},$$

where $\Psi \equiv (K_H S M/M_S + g\mu_B H) f(n^\alpha)$, $\sigma = 1/2(-1/2)$ for spin $\alpha = \uparrow (\downarrow)$ holes and

$$\epsilon_{\vec{k}}^\alpha = 2\tilde{t} h(\delta) f(n^\alpha) \sum_l \cos(k_l^\alpha a) << k_B T_C. \quad (13)$$

In the above equation $h(\delta) = 1 - \delta$ and T_C is the ferromagnetic transition temperature whose value, by treating M and $\Delta n \equiv n^\uparrow - n^\downarrow$ as small parameters in Eq. (12), is obtained to be

$$k_B T_C = \sqrt{\frac{20(1-\delta)\delta}{9(2-\delta)^2}} K_H S |\sigma|. \quad (14)$$

We see that T_C increases with increasing δ for $0 < \delta < 2/3$ and that it is independent of both t and J_{ij}. Furthermore because of Eq. (13) the values of M, n^α, and T_C are all independent of dimensions [see Eq. (12)]. Here it must also be mentioned that when double occupancy is allowed $h(\delta) = f(n^{\uparrow(\downarrow)}) = 1$.

Using the constraint that $n^\uparrow + n^\downarrow = \delta$, we can obtain Δn and M by solving Eq. (12). In Fig. 1 we have plotted the magnetization ratio M/M_S as a function of the reduced temperature T/T_C for $\delta = 0.3$ and 0.4, $g = 2$, and magnetic fields $H = 0T$ and $15T$. We have assumed a smaller value for the Hund's coupling ($K_H \approx 0.0858eV$) than what seems to be its value based on experiments ($\sim 1eV$) because we wanted to set $T_C = 300K$ at $\delta = 0.3$. Alternately one can also get lower T_C by assuming, as suggested in Ref. [5], that only a small fraction of the dopants yield mobile holes. The values of the magnetization for $H = 15T$ at T_C are sizeable because of the tendency of the system towards a ferromagnetic phase. Here it should also be mentioned that Δn attains saturation values much faster than M [15]. We have also calculated the magnetization curves with double occupation of a site being allowed and find that the M/M_S values for with and without double occupation being allowed are close to each other both in zero field and at $15T$ [15]. Although our magnetization curves are qualitatively similar to the experimental curves of Urushibara et al. [10], the experimental M/M_S values rise faster as T is lowered.

We will now discuss the resistivity given by Eq. (10). The conduction goes from a hopping type at high temperatures to a band type at low temperatures. In Fig. 2 we have shown the dependence of resistivity ρ on temperature at various magnetic fields. The general trend of the resistivity including the drop at the MI transition at $H = 0T$ is similar to the experimental results [10]. On introducing a magnetic field the system gets magnetized at temperatures higher than T_C and thus the value of θ is smaller (see Eq. (10)). Consequently the resistivity is smaller and $T_{\rho^{max}}$ (the temperature at which resistivity becomes maximum) increases [16].

For $T \geq T_C$, when $D_{band}/D_{hop} >> 1$ the magnetoresistance $\Delta\rho/\rho(0) \equiv (\rho(H) - \rho(0))/\rho(0)$ is given by (see Eq. (10))

$$\Delta\rho/\rho(0) \approx \exp\left[-\frac{(z+1)}{2\gamma^2}\frac{t^2}{\omega_0^2}\frac{M^2}{M_S^2}\mathrm{csch}(\frac{\beta\omega_0}{2})\right] - 1, \quad (15)$$

and when $D_{band}/D_{hop} << 1$ it is given by

$$\Delta\rho/\rho(0) \approx \frac{\exp\left[-\frac{(z+1)}{2\gamma^2}\frac{t^2}{\omega_0^2}\frac{M^2}{M_S^2}\tanh(\frac{\beta\omega_0}{4})\right]}{1 + (M/M_S)^2} - 1. \quad (16)$$

For a fixed value of the reduced temperature T/T_C, an increase in the ratio $\mu_B H/K_H$ increases M/M_S and consequently the magnetoresistance also increases.

Actually $T_{\rho^{max}_{M=0}}$ (the temperature at which the resistivity given by Eq. (10), after taking $M = 0$, attains a maximum) need not be equal to the ferromagnetic transition temperature T_C. If $T_{\rho^{max}_{M=0}} < T_C$, by decreasing γ^2 or increasing $\frac{t^2}{\omega_0^2}$ activation energy ($\theta\omega_0/2$) decreases and $T_{\rho^{max}_{M=0}}$ can be increased [16] to be made equal to T_C and this also increases the magnetoresistance (see Eqs. (10), (15), and (16)). For $T_{\rho^{max}_{M=0}} < T_C$, the MI transition can still occur at T_C if $\frac{(z+1)}{2\gamma^2}\frac{t^2}{\omega_0^2}$ is sufficiently large [16] while if $\frac{(z+1)}{2\gamma^2}\frac{t^2}{\omega_0^2}$ is very small the MI transition occurs below $T_{\rho^{max}_{M=0}}$ as can be seen from Eq. (10). The other case, where $T_{\rho^{max}_{M=0}} > T_C$, corresponds to MI transition occurring at a higher temperature than T_C and is in any case not experimentally observed [15].

In Table I we report the calculated values of magnetoresistance $-\Delta\rho/\rho(0)$ at T_C and the optimum values of γ^2 (obtained when $T_{\rho^{max}_{M=0}} = T_C$) for doping δ equal to 0.3 and 0.4, Debye temperature $T_D = 500K$, and for various values of the dimensionless hopping integral t/ω_0. We find that the magnetoresistance increases with increasing values of t/ω_0 thus showing the importance of bandwidth. Also γ^2_{opt} values increase with increasing t/ω_0 because $T_{\rho^{max}_{M=0}} = T_C$. Furthermore, it is mainly due to the larger values of $(M/M_S)^2$ for $\delta = 0.4$ compared to those of $\delta = 0.3$ that the values of $-\Delta\rho/\rho(0)$ are larger for $\delta = 0.4$. It appears that our model can give magnetoresistance values comparable to the experimental ones [10]. In fact one can get a larger magnetoresistance by taking a smaller T_C value but keeping $\omega_0/(k_B T_C)$ fixed [15].

From Eq. (10) (or Eqs. (15) and (16)) we see that for small values of M/M_S the magnetoresistance (for $T \geq T_C$) is of the form $-\Delta\rho/\rho(0) = C(M/M_S)^2$ where C is a constant of proportionality. We found, for the cases considered in Table 1, that the optimum values of γ^2 that make $T_{\rho^{max}_{M=0}} = T_C$ are such that $D_{band}/D_{hop} < 1$ so that the magnetoresistance can be qualitatively given by Eq. (16). In Eq. (16), close to T_C, $\tanh(\beta\omega_0/4) \approx \beta\omega_0/4$. From Eq. (14) we see that T_C increases with the doping δ and hence the constant of proportionality C ($\propto \frac{(2-\delta)}{\sqrt{(1-\delta)\delta}}$) decreases with increasing δ which agrees with the findings of Ref. [10]. Furthermore the coefficient also increases with increasing values of $\frac{(z+1)t^2}{\gamma^2 T_C \omega_0}$. We have calculated values of C by treating M/M_S as a small parameter in the exact expression for $-\Delta\rho/\rho(0)$ at $T = T_C$. When $t/\omega_0 = 4(8)$ and $\gamma^2 = 9.5(15.0)$, for $\delta = 0.3$ we get $C \approx 3.8(8.5)$ while for $\delta = 0.4$ we obtain $C \approx 3.1(6.4)$. Our calculated values of C are larger than those reported in Ref. [10]. Past attention [17,18] has focused at dependence of C on the ratio K_H/t in Kondo lattice type models that ignored electron-phonon coupling. While Inoue and Maekawa [17] for $K_H \to \infty$ obtained $C = 7/4$, Furukawa [18] found that the value of C increased with

increasing values of K_H/t and that at larger values of K_H/t the value of C decreases with increasing doping.

In conclusion we say that both double exchange and finite band-width corrections are important to understand CMR. In our picture, adiabatic small-but-sizeable magnetic polarons are involved in activated transport at high temperatures and metal-like conduction at low temperatures. At the MI transition, the band-like motion of the carriers also produces a paramagnetic-ferromagnetic transition due to strong Hund's coupling between itinerant and localized spins. Studying the transport behavior at low temperatures, including a Fermi liquid analysis, is left for future. The effect of including both $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals also needs to be investigated for our model. Lastly we note that as the system's temperature is lowered below T_C the magnetization increases and consequently the activation energy ($\theta\omega_0/2$) decreases and the polarons tend towards large polaronic behavior.

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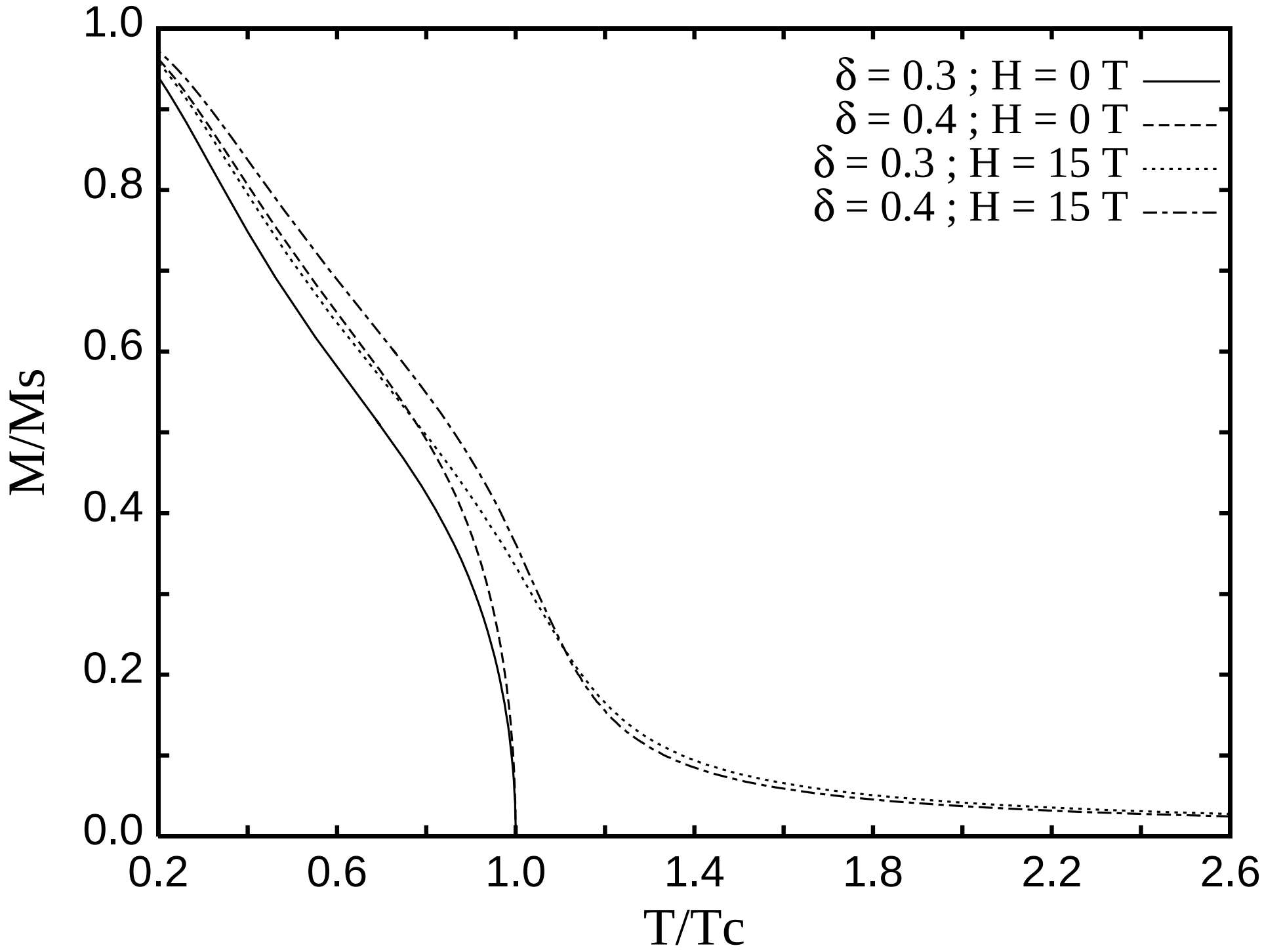
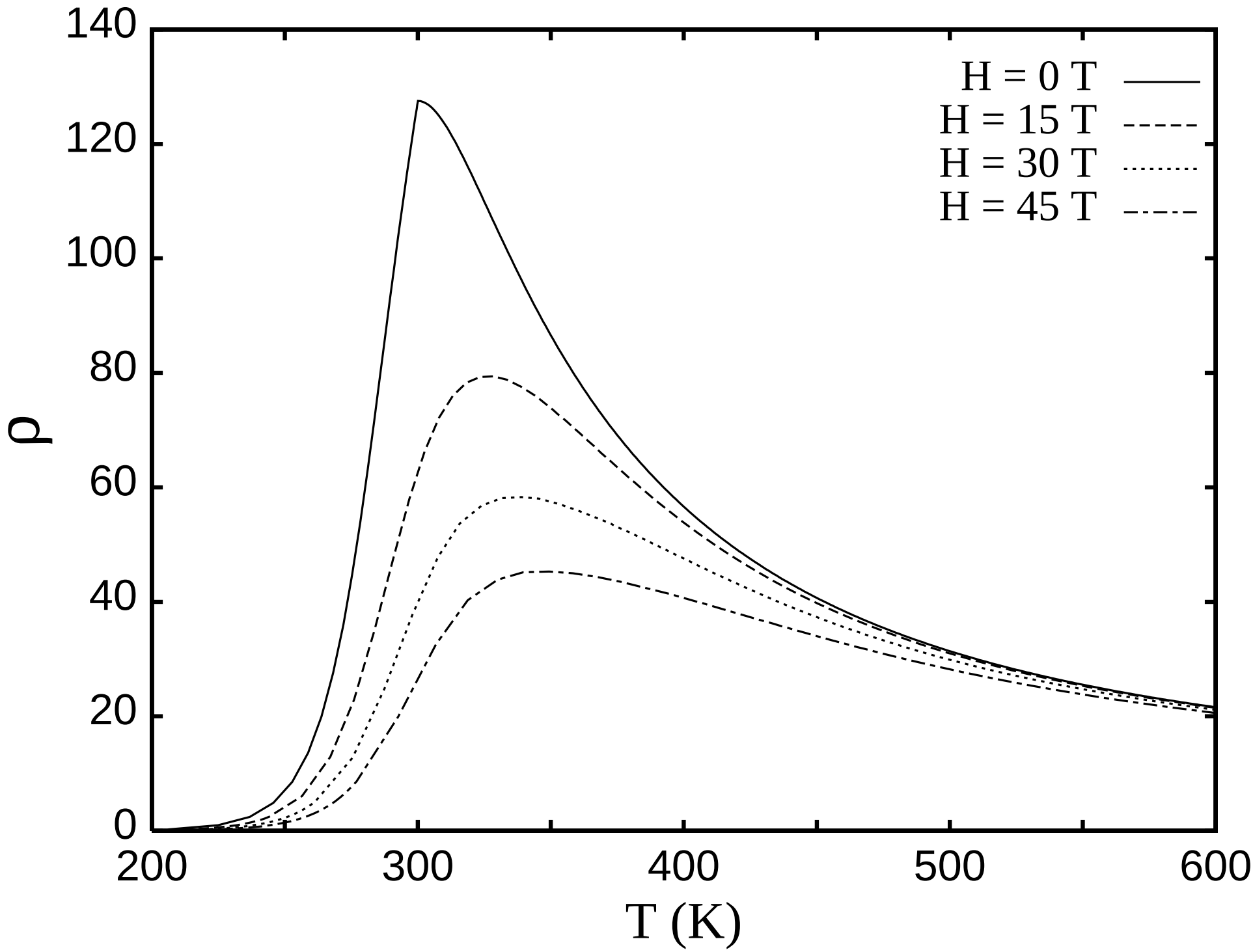
FIG. 1. Plot of the magnetization ratio M/M_S versus the reduced temperature T/T_C when no double occupation is allowed, doping $\delta = 0.3$ (and 0.4), Hund's coupling $K_H \approx 0.0858eV$, and magnetic fields $H = 0T$ and $H = 15T$.

FIG. 2. Plot of the resistivity ρ in units of $4\pi/(c_h q_e^2 a^2)$ versus temperature T in 3 dimensions when no double occupation is allowed, $\delta = 0.3$, $K_H \approx 0.0858eV$, dimensionless hopping integral $t/\omega_0 = 6$, optimum $\gamma^2 = 12.2$, Debye temperature $T_D = 500K$, and for the following magnetic fields: (i) $H = 0T$; (ii) $H = 15T$; (iii) $H = 30T$; and (iv) $H = 45T$.

TABLE I. Calculated values of the magnetoresistance $-\Delta\rho/\rho(0)$ at T_C and the optimum γ^2 for various values of t/ω_0, $T_D = 500K$, $\delta = 0.3$ and 0.4, magnetic field $H = 15T$, $K_H \approx 0.0858eV$, and $T_{\rho_{M=0}^{max}} = T_C$.

	$\delta = 0.3$; $T_C = 300K$		$\delta = 0.4$; $T_C \approx 341K$	
t/ω_0	γ^2_{opt}	$\frac{-\Delta\rho}{\rho(0)}$	γ^2_{opt}	$\frac{-\Delta\rho}{\rho(0)}$
4	9.5	35%	8.4	42%
5	10.8	44%	9.8	50%
6	12.2	51%	11.2	58%
7	13.6	58%	12.5	68%
8	15.0	64%	13.9	74%


δ = 0.3 ; H = 0 T
δ = 0.4 ; H = 0 T
δ = 0.3 ; H = 15 T
δ = 0.4 ; H = 15 T
M/Ms
T/Tc
1.0
0.8
0.6
0.4
0.2
0.0
0.2
0.6
1.0
1.4
1.8
2.2
2.6


140
120
100
80
60
40
20
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ρ
200
300
400
500
600
T (K)
H = 0 T
H = 15 T
H = 30 T
H = 45 T